



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07F 17/00, C08F 10/00, C07F 7/08, 7/10, 5/02, C07D 495/04, 487/04, 333/78, 317/70, C07F 9/6568	A1	(11) International Publication Number: WO 98/22486 (43) International Publication Date: 28 May 1998 (28.05.98)
(21) International Application Number: PCT/EP97/06297 (22) International Filing Date: 12 November 1997 (12.11.97) (30) Priority Data: 96118369.6 15 November 1996 (15.11.96) EP (34) Countries for which the regional or international application was filed: NL et al. (71) Applicant (for all designated States except US): MONTELL TECHNOLOGY COMPANY B.V. [NL/NL]; Hoeksteen 66, NL-2132 MS Hoofddorp (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): EWEN, John, A. [US/US]; 14311 Golf View Trail, Houston, TX 77059 (US). ELDER, Michael, J. [US/IT]; Corso della Giovecca, 140, I-44100 Ferrara (IT). JONES, Robert, L., Jr. [US/IT]; Via Carlo Mayr, 110, I-44100 Ferrara (IT). DUBITSKY, Yuri, A. [RU/IT]; Via Valassina, 45, I-20159 Milano (IT). (74) Agents: ZANOLI, Enrico; Montell Italia S.p.A., Intellectual Property, Via Pergolesi, 25, I-20124 Milano (IT) et al.		(81) Designated States: AU, BR, CA, CN, CZ, HU, ID, IL, JP, KR, MX, NO, PL, RU, SG, TR, US, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. RECEIVED JAN 23 2002 TC 1700
(54) Title: HETEROCYCLIC METALLOCENES AND POLYMERIZATION CATALYSTS (57) Abstract A new class of heterocyclic metallocenes, a catalytic system containing them and a process for polymerizing addition polymerizable monomers using said catalytic system are disclosed; the heterocyclic metallocenes correspond to the formula (I): $Y_iR''^iZ_{jj}MeQ_kP_l$ wherein Y is a coordinating group containing a six π electron central radical directly coordinating Me, to which are associated one or more radicals containing at least one non-carbon atom selected from B, N, O, Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te; R'' is a divalent bridge between the Y and Z groups; Z is a coordinating group, optionally being equal to Y; Me is a transition metal; Q is halogen or hydrocarbon substituents; P is a counterion; i is 0 or 1; j is 1-3; jj is 0-2; k is 1-3; and l is 0-2.		

HETEROCYCLIC METALLOCENES AND POLYMERIZATION CATALYSTS**FIELD OF THE INVENTION**

The present invention relates to new heterocyclic metallocenes and to catalytic systems for the production of homopolymers and copolymers having a wide range of properties, including linear low density, high density, atactic, isotactic and syndiotactic polymers.

More particularly, this invention relates to a new class of metallocenes containing at least one heteroatom in a ring system associated with a six π electron central radical directly coordinating a transition metal, said metallocene being capable of polymerizing addition polymerizable monomers.

BACKGROUND OF THE INVENTION

Polymerization of vinyl monomers, both mono-olefins and conjugated dienes, has focused on transition metal catalysts since the work of Ziegler and Natta. These catalysts are based on a central transition metal ion or atom surrounded by a set of coordinating ligands and modified by various cocatalysts.

By controlling the nature of the ligand system, the central transition metal ion or atom, and the co-catalyst, highly active catalytic agents can be made. In addition, catalysts can be made that yield polymers with high degrees of addition regularity, and in the case of non-ethylene type monomers, stereoregular or tactioselective and/or tactiospecific polymers can be made.

U.S. Pat. No. 3,051,690 discloses a process of polymerizing olefins to controlled high molecular weight polymers by the controlled addition of hydrogen to a polymerization system that includes a hydrocarbon insoluble reaction product of a Group IVB, VB, VIB and VIII compound and an alkali metal, alkaline earth metal, zinc, earth metal or rare earth metal organometallic compound. It is further known that certain metallocenes, such as bis(cyclopentadienyl) titanium or zirconium dialkyls, in combination with aluminum alkyl/water cocatalysts, form homogeneous catalyst systems for the polymerization of ethylene.

German Patent Application 2,608,863 discloses the use of a catalyst system for the polymerization of ethylene, consisting of bis(cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water. Furthermore, German Patent Application 2,608,933 discloses an ethylene polymerization catalyst system including a catalyst of general formula $(Cp)_nZrY_{4-n}$, where n is a number from 1 to 4 and Y is a hydrocarbon group or a metallocyl in combination with an aluminum trialkyl cocatalyst and water (Cp indicates cyclopentadienyl).

European Patent Appl. No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system of general formula $(Cp)_nMeY_{4-n}$, where n is an integer from 1 to 4, Me is a transition metal, especially zirconium, and Y is either

hydrogen, a C₁-C₅ alkyl, a metalloalkyl group or other radical, in combination with an alumoxane.

U.S. Patent No. 5,324,800 discloses a catalyst system for polymerizing olefins including a metallocene catalyst of general formula $(C_5R'_m)_p R''_s (C_5R'_m) MeQ_{3-p}$ or $R''_s (C_5R'_m)_2 MeQ'$, where $(C_5R'_m)$ is a substituted Cp group, and an alumoxane.

Polyolefins can be prepared in a variety of configurations that correspond to the manner in which each new monomer unit is added to a growing polyolefin chain. For non-ethylene-polyolefins four basic configurations are commonly recognized, i.e. atactic, hemi-isotactic, isotactic and syndiotactic.

A given polymer may incorporate regions of each configurational type, not exhibiting the pure or nearly pure configuration.

On the opposite polymers of monomers symmetrically equivalent to ethylene (i.e., the 1,1 substituents are identical and the 2,2 substituents are identical, sometimes referred to as "ethylene-like monomers") can have no tacticity.

Atactic polymers exhibit no regular order of repeat unit orientation in the polymer chain, i.e. the substituents are not regularly ordered relative to a hypothetical plane containing the polymer backbone (the plane is oriented such that the substituents on the pseudo-asymmetric carbon atoms are either above or below the plane). Instead, atactic polymers exhibit a random distribution of substituent orientations.

Additionally, other type of catalyst belonging to the family of metallocene catalyst are the so-called "constrained geometry catalysts", where one of the cyclopentadienyl groups has been replaced by a heteroatom ligand, such as an amino or phosphino anion. Such catalysts are described in United States Patents No: 5,453,410, 5,399,635, and 5,350,723.

Besides metallocene catalyst that produce polyethylene and atactic polyolefins, certain metallocenes are also known to produce polymers with varying degrees of stereoregularity or tacticity, such as isotactic, syndiotactic, and hemi-isotactic polymers, which have unique and regularly repeating stereochemistries or substituent orientations relative to the plane containing the polymer backbone.

Isotactic polymers have the substituents attached to the asymmetric carbon atoms oriented on the same side, relative to the polymer backbone, i.e. the substituents are all either configured above or below the plane containing the polymer backbone. Isotacticity can be determined through the use of NMR. In conventional NMR nomenclature, an isotactic pentad is represented by "mmmm" where each "m" represents a "meso" dyad or successive monomer units having the substituents oriented on the same side relative to the polymer backbone. As is well known in the art, any inversion of a pseudo-asymmetric carbon in the chain lowers the degree of isotacticity and crystallinity of the polymer.

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference TC 5421 ASC	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/EP 00/13192	International filing date (day/month/year) 22/12/2000	(Earliest) Priority Date (day/month/year) 28/12/1999
Applicant BASELL TECHNOLOGY COMPANY B.V. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

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1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☒ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. -

- ☐ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.
- ☒ None of the figures.

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

As a result of the prior review under R. 40.2(e) PCT,
all additional fees are to be refunded.

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

1-15,22,25,26
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☒ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-15

Process for the preparation of polymers of ethylene with a metallocene catalyst

2. Claims: 16-17

Process for the preparation of a ligand

3. Claim : 18

Process for preparing a pre-ligand of formula (III)

4. Claim : 19

Process for the preparation of a pre-ligand of formula (III)

5. Claims: 20-21

Process for the preparation of a pre-ligand of formula (III)

6. Claim : 22

Process for the preparation of a metallocene compound of formula (I)

7. Claim : 23

Process for the preparation of a pre-ligand of formula (III)

8. Claim : 24

A pre-ligand of formula (III)

9. Claim : 25

A metallocene compound of formula (I)

10. Claim : 26

A ligand of formula (II)

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F10/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 22486 A (JONES ROBERT L JR ;DUBITSKY YURI A (IT); ELDER MICHAEL J (IT); MON) 28 May 1998 (1998-05-28) cited in the application	1-15,25, 26
X	page 32-33; claim 9; examples 6-10	22
A	EWEN J A ET AL: "POLYMERIZATION CATALYSTS WITH CYCLOPENTADIENYL LIGANDS RING-FUSED TO PYRROLE AND THIOPHENE HETEROCYCLES" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY,US,AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, vol. 120, 1998, pages 10786-10787, XP000907012 ISSN: 0002-7863 the whole document	1-15,22, 25,26

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 August 2001

Date of mailing of the international search report

22 Aug

Name and mailing address of the ISA

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9822486 A	28-05-1998	AU 733813 B	24-05-2001
		AU 5321698 A	10-06-1998
		BR 9715006 A	05-12-2000
		CN 1244201 A	09-02-2000
		EP 0938491 A	01-09-1999
		HU 9904527 A	28-05-2000
		JP 2001504824 T	10-04-2001
		NO 992352 A	08-07-1999
		PL 333462 A	20-12-1999
		TR 9901635 T	21-02-2000
		TW 394779 B	21-06-2000
